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MODELING VALIDATION, TECHNIQUES AND APPLICATIONS FOR X-RAY LITHOGRAPHY

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ABSTRACT

The experimental development of soft X-ray lithography in conjunction with fabrication of blazed diffraction gratings is discussed. Interferometrically produced gold masks on thin silicon windows and a technique for protecting the mask during etching of the window are described. Images resulting from a multiple source angle exposure technique are shown in support of this technique as a workable concept. Prints of Ni grids and submicron period Au gratings on thin silicon windows are also shown. The constructive use of thermal effects during both exposure and development are also considered.

I. INTRODUCTION

In an earlier publication [1], the feasibility of producing blazed diffraction gratings with X-ray lithography was explored. This work as motivated by the desire for better grating groove shapes and the possibility of using a single mesh to replicate gratings with a variety of blaze angles. It was shown [1] that soft X-ray contact printing with a columnated beam appears quite promising for producing deep blazed gratings with up to 10,000 lines/mm. Initial experimental technique were based on the X-ray lithography techniques described by D. L. Spears et al. [2]. The process was modified and new techniques have been developed in order to accomplish our goals within the framework of our laboratory research facilities.

II. MASK FABRICATION

X-ray masks have been fabricated by placing gold patterns on thin silicon windows as described by Mccoy and Sullivan [3], and by Cohen et al. [4]. Here we describe the process used in our laboratory and in particular those steps that differ from those described elsewhere [3] [4].

The first step in mask fabrication is the diffusion of Boron into the front surface of <100> n-type 3-cm diameter silicon wafer. This is done at a temperature of 1100°C in a flowing gas atmosphere of B_2H_6,O_2 and N_2 for 6 hours. The membrane thickness obtained after preferential etching is around 3 μm. Drive-in at a temperature of 950°C in a wet atmosphere for 3 hours with subsequent etching in concentrated HF will remove the boron glass. A 12000 Å film of SiO_2 is sputter deposited on back side of the wafer and a 1500 Å film, again of SiO_2, is deposited on the front side. A thin layer of Nichrome (300 Å) is then evaporated on the front surface followed by the evaporation of a 2000 Å

gold film.

The wafer is then coated with 3000 Å of Shipley AZ1350J positive photoresist and exposed interferometrically using a Helium-Cadium laser (3250 Å wavelength). After exposure, the pattern unit is developed in a 1:1 solution of AZ1350 developer and water. For a 14 minute exposure, at a total laser power output of .4 mW, the development time is 30 seconds. The subsequent postbaking of the developed resist profile is critical for two reasons: The resist has to hold and not flow during r.f. sputter etching. This requires a rather elevated postbaking temperature. Also the preservation of the developed resist profile (a submicron period grating structure) during postbaking imposes the opposite requirement, i.e. a low postbaking temperature. We chose a two step process where we postbake for a while at a low temperature (90°C) and immediately afterwards at a higher temperature (110°C).

Both r.f. sputter etching and wet (chemical) etching have been used to produce the gold pattern on the front side of the wafer; however, due to edge resolution and undercutting of chemical etching r.f. sputter etching is preferred over chemical etching. Figures 1 and 2 show a typical mask after r.f. sputter etching. The roughness of the lines is apparently due to roughness in the developed photoresist surface.

A major fabricational problem was encountered due to the fact that the preferential etchant of silicon (ethylenediamine pyrochatechol-water) would attack the gold surface. The gold would acquire a frosty appearance after several hours in the etching solution and the grating lines would be literally ripped off. Two alternative procedures were examined.

The first one, proposed by Bernacki et al. [4] was to use a teflon fixture so that only one side of the wafer is in contact with the etchant. However our fixture could only accomodate a certain size circular wafer, and it was difficult to handle a variety of wafer sizes and pieces of various shapes.

Another procedure was to open the window first and then deposit the gold mask. The difficulty of this approach was that the handling of the wafer through the remaining process steps had to be extremely careful.

A variety of different resist and wax films were tried for protection during etching, but they were almost immediately lifted off upon immersion in the etching solution. One known material that etches very slowly is SiO_2; therefore, it was decided to use SiO_2 as a protective film. To this end, the remaining mask fabrication steps are as follows:

1) Evaporate 300 Å of Nichrome on the gold relief structure. This thin film is used as a convenient adhesive interface between gold and SiO_2.

2) Sputter deposit a 1.2 μm film of SiO_2 on top of the Nichrome. This film will protect the gold pattern during the preferential etching of silicon.

3) Coat both sides of the wafer with AZ1350J and then open a SiO_2 window on the back side of the wafer, directly beneath the gold pattern The SiO_2 window is 7.5 mm square.

4) The wafer is then immersed in the preferential etchant and upon etching of the silicon up to the boron doped layer, the wafer is removed from the solution, placed in warm methanol, then rinsed in DI H_2O and blown dry.

5) The SiO_2 films on both sides of the wafer are then removed by immersion of the wafer in buffered HF.

6) The thin Nichrome film may be left on top of the gold pattern or etched with dilute HCl.

A sketch of the topology for this process is shown in Figure 3.

III. EXPOSURE DEPENDENT RESIST PROPERTIES

The X-ray exposure system consists of a horizontal evaporation gun and a water cooled target at angle of 45° with interchangeable target material. The electron beam diameter size is 4 mm and the target is capable of dissipating the heat produced by a 200 mA current beam. Typical exposure parameters are a beam current of 100 mA, a source to substrate distance of 8 cm and one hour exposure time. Due to equipment availability the above exposure system together with the mask substrate holder had to be incorporated as a unit in one vacuum system. This imposes a severe limitation on exposure time because of the amount of heat generated by the gun cathode filament and the unavailability of suitable conduction or convection paths for efficient cooling of the mask substrate system. Heat is generally detrimental but in some particular instance it can be beneficial. In particular we noted that the pattern was visible in some cases immediately after exposure. The explanation is related to the type of scission events taking place during exposure.

It is well known that PMMA exhibits predominantly random chain scission upon X-ray exposure with a subsequent decrease in the initial average molecular weight. The final average molecular weight after exposure is inversely proportional to the radiochemical yield G for main chain fracture. It has been shown that G increases with temperature. This can be utilized so that exposure time may be decreased in typical X-ray lithographic applications by increasing the ambient temperature of the X-ray exposure system or by incorporating small amounts of acrylonitrile in the PMMA resist [5].

Polymers used for X-ray resists are also degrated by other types of processes such as thermal degradation (Pyrolysis) [6]. Thermal degradation can be divided roughly into two general categories: random chain scission and depolymerization. The latter is essentially a depolymerization process in which monomer units release from the chain ends. In this type of degradation the molecular weight of the residual polymer remains almost equal to the initial average molecular weight.

For low average molecular weight PMMA thermal degradation consists almost exclusively of depolymerization. Volatile monomer (methyl-methacrylate) is almost the exclusive product [7]. The simultaneous radiation degradation and thermal depolymerization can be useful in X-ray lithography since X-ray-thermal exposure is effectively a simultaneous exposure and development process.

IV. EXPOSURE RESULTS

Commercially available nickel grids with 10 μm and 6 μm linewidth were contact printed in PMMA on flexible glass. As it was mentioned earlier, we noted that profiles were visible in some cases immediately after exposure; however the contrast was low. Subsequent development in a mixture of 60% isopropyl alcohol and 40% isobutyle keytone for 50 minutes increased the contrast substantially by deepening the pattern in the exposed regions. This validated the simultaneous radiation degradation and thermal depolymerization effect.

The 10 μm grid was also contact printed in PMMA using a two source exposure as follows: first the mask substrate system was positioned at an angle of 35° with respect to the horizontal and exposed for 20 minutes at a source to substrate distance of 8 cm and a beam current of 100 mA. Then the mask substrate system was rotated around its axis of rotation so that the angle for the second case was -55°. It was again exposed for the same time.

This exposure scheme produced three distinct regions of exposure.

A. A region where the exposure was maximum (effectively a 40 minute exposure).

B. A region where one exposure was partially attenuated to the mask.

C. A region where both exposures were partially attenuated.

The results after development in Figure 4 show a distinct 3 step structure due to the different etch rates in the different regions of exposure. The visible edge ripple of the replicated grid bars is due to the exact reproduction of the origin of Nickle mask which had rippled edges.

Next a submicron gold grating on top of a thin silicon window was replicated at an angle of 10°. The diameter of the grating area was

6 mm. Due to the penumbra the grooves of the replicated grating in PMMA shown in Figure 5 are wider than the originals of the gold grating. Also, limitation in exposure time (One hour total exposure time at 100 mA beam current at source to substrate distance of 6 cm) due to excessive heating of the mask substrate system, resulted in poor contrast after development. Total development time was 50 min in a 60:40 mixture of IPA:MIBK. The eventual goal is the control of replicated grating groove shape through the use of a multiple angle exposure technique as depicted in Figure 6.

V. CONCLUSIONS

The feasibility of X-ray lithographic fabrication of blazed diffraction gratings has been explored experimentally through development of interferometrically produced masks and multiple source angle exposures. Gold masks with a .6 μ period on a 7.5 mm square 3 μ thick silicon window were produced using the 3250 Å line of a He-Cd laser, positive photoresist (AZ1350J), and r.f. sputter etching. A nichrome and SiO_2 coating technique was developed for protecting the gold mask during the etching of the thin silicon window.

Replication was accomplished with a $Al_{K\alpha}$ line (8.3 Å) exposure system. During exposure additional thermal effects were noted and explored theoretically. These effects were generally detrimental, but sometimes useful as in the case of replicating nickel grids. A two angle exposure produced images which established the multiple source exposure technique as a workable concept. The .6 μ period gratings were successfully replicated; however, due to our exposure system limitations the extent to which the replicated grating groove shape can be controlled is a bit uncertain.

ACKNOWLEDGEMENT

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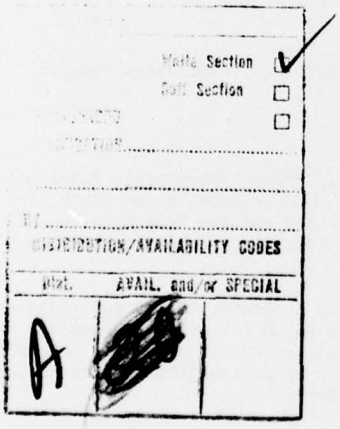

Fig. 1 Gold mask on thin silicon window produced by r.f. sputter etching interferometrically exposed AZ1350J at 3250Å.

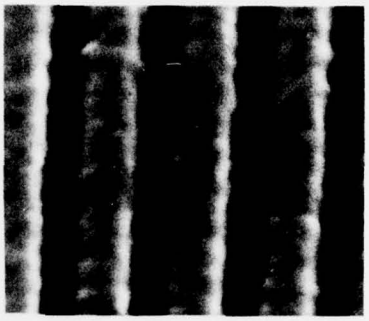

Fig. 2 Close up of gold mask showing roughness apparently related to developed photoresist roughness.

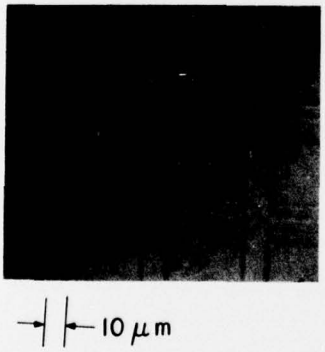

Fig. 4 Replication of 10 μ nickel grid in PMMA showing superpositions of two images made through the use of exposures at two source angles.

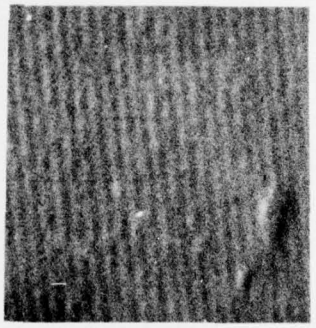

Fig. 5 Replication-.6 μ period grating in PMMA.

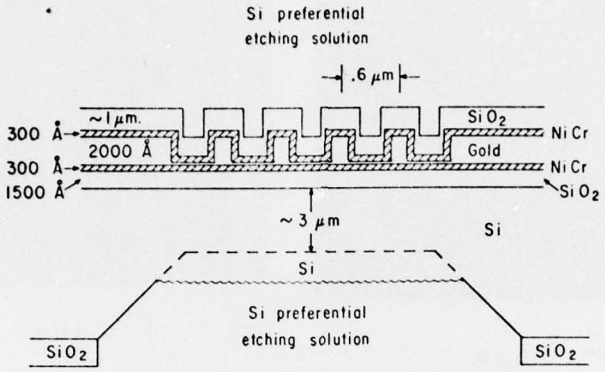

Fig. 3 Wafer topology for nichrome-SiO_2 protection of Au mask during window etching.

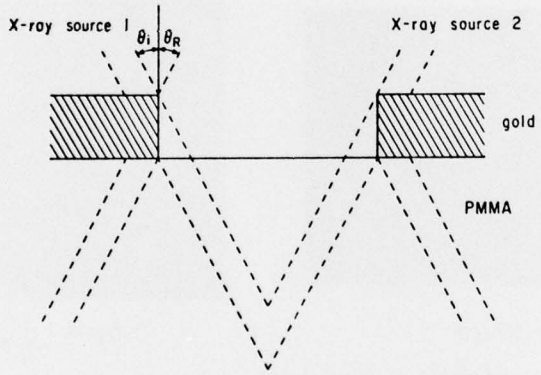

Fig. 6 Multiple angle exposure technique for groove shape control.

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